WO 99/37733
TO/PCT Rec'd 27 JAN 2000
09/463598
PCT/SE99/00086

Frost resistant heating/cooling fluid

Technical field

The present invention relates to a frost resistant, aqueous heating/cooling fluid, containing alkali salts of acetic acid and/or formic acid. The heating/cooling fluid is intended for transport of cold or heat in industrial cooling plants, cooling systems in vessels and vehicles, cooling systems for skating ice in sports centres, heat exchangers, district heating systems, heat pumps, solar panels etc.

Background of the invention

In aqueous heating/cooling fluids, frost resistance is usually obtained by means of an addition of ethylene glycol. Ethylene glycol is a liquid which is mixable with water to any extent, exhibits a low risk of fire and explosion, and is frost resistant and also colourless and odourless. The lowest solidifying point (-57 °C) of a glycol-water mixture is at a ethylene glycol content of 60 volume-%. However, the disadvantage with ethylene glycol is its high degree of toxicity. Thereby, it poses an environmental threat if it ends up in the sea, lakes and streams, for instance, if cooling liquid is discharged or leaks out.

From EP-B-0 306 972, a partially or completely glycol-free, aqueous cooling fluid is known, which contains an addition of sodium acetate and sodium formate or potassium acetate and potassium formate in certain ratios. By means of this fluid composition, a freezing temperature pf -70 °C or lower can be obtained. The fluid composition exhibits all the advantages with the conventional glycol-water mixture, at the same time as it does not exhibit its toxicity.

However, the above-mentioned cooling fluid contains strong ions, wherein it is very important to have a good corrosion protection. In EP-B-0 306 972, it is disclosed that benzoic acid, sodium benzoate, potassium benzoate or benzotriazole are used for corrosion

protection. These are film-forming chemicals. The formed film protects metal surfaces from corrosion attacks. In order not to risk local corrosion attacks, the film layer has to be intact across the entire metal surface. A disadvantage with the film is an impaired heat transfer between the metal surface and the cooling fluid.

Purpose of the invention and most important features

The purpose of the present invention is to provide a corrosion protected heating/cooling fluid of the above-mentioned type, which exhibits an effective heat transfer between metal surface and fluid, at the same time as the corrosion protection is excellent. This has been achieved by means of the fluid containing a corrosion inhibitor in the form of a mixture of a C_5-C_{16} monocarboxylic acid or alkali-, ammonium- or amino-salts of said acid, a C_5-C_{16} dicarboxylic acid or alkali-, ammonium- or amino-salts of said acid, and also a triazole.

The content of alkali salts of acetic acid and/or formic acid in the heating/cooling fluid should preferably be between 5 and 50 weight-%, calculated on the total weight of the fluid.

The heating/cooling fluid contains between 0.4 and 10 weight-%, preferably between 0.5 and 2 weight-% of the above-mentioned corrosion inhibitor, calculated on the total weight of the alkali salts of acetic acid and/or formic acid.

Summary of the invention

From the above-mentioned EP-B-0 306 972, it is known that an addition of alkali salts of certain anions, mainly acetates and formates, to water results in a strong depression of freezing-point of an aqueous medium. The depression of freezing-point becomes particularly large at certain mixing ratios of the included salts.

The heating/cooling fluid according to the invention contains between 5 and 50 weight-% alkali salts of acetic acid and/or formic acid calculated on the weight of the fluid, primarily sodium acetate, potassium acetate, sodium formate and/or potassium formate. The included salts can be present in any mutual mixing ratio, i.e. only one of the salts or two or several salts in a mixture together. Partly depending on the total salt content, and partly on the

mixing ratio of the salts, different depressions of freezing-point of the fluid is obtained. Also other freezing-point depressing additions can be included in the fluid, e.g. urea.

The heating/cooling fluid according to the invention is a strong ionic solution, wherein the significance of an efficient corrosion protection is particulary large. EP-B-0 306 972 discloses an addition of a corrosion inhibitor in the form of benzoic acid, sodium benzoate, potassium benzoate or benzotriazole, which are film-forming chemicals which create a protective film on metals surfaces and thereby protects them from corrosion attacks. As mentioned above, the disadvantages with this type of corrosion inhibitors is partly that the film layer must be intact across the entire metal surface in order to make the corrosion protection effective and to avoid local corrosion attacks, and partly that the heat transfer between metal surface and heating/cooling fluid is impaired.

According to the invention, it has now surprisingly been found that, in addition to an excellent corrosion protection, an addition of a corrosion inhibitor in the form of a mixture of a C_5-C_{16} monocarboxylic acid or alkali-, ammonium- or amino-salts of said acid, and also a triazole, furthermore provides an excellent heat transfer between the metal surface and the fluid.

A corrosion inhibitor of this type is disclosed in US-A-4,647,392. According to this document, the corrosion inhibitor is intended to be used in glycol-water mixtures. The use as a corrosion inhibitor in salt solutions of the type which the invention relates to, however, is not disclosed in the U.S. patent.

The amounts of the components included in the corrosion inhibitor can vary between 0.02 and 3 weight-%, calculated on the weight of the fluid, for both the monocarboxylic acid and the dicarboxylic acid or the alkali-, ammonium-, or amino-salts of said acid. The amount of triazole can vary between 0.02 and 2 weight-%, calculated on the total weight of the fluid.

The total content of the corrosion inhibitor should be between 0.4 and 10 weight-%, preferably between 0.5 and 2 weight-%, calculated on the weight of the fluid.

The corrosion inhibitor comprises a mixture of three basic components, namely a monocarboxylic acid, a dicarboxylic acid and a triazole. The monocarboxylic acid is preferably an aliphatic C_5-C_{16} monocarboxylic acid, preferably selected from the group of octanoic acid, nonaic acid, decanoic acid, undecanoic acid or dodecanoic acid, 2-ethyl hexanoic acid and neodecanoic acid.

The dicarboxylic acid is preferably either a C_8-C_{12} aliphatic dicarboxylic acid selected from the group of suberic acid, azealic acid, sebacic acid, undecanoic di-acid, dodecanoic di-acid and the di-acid of di-cyclopentadienylide or a C_8-C_{12} aromatic dicarboxylic acid, preferably terephthalic acid.

The triazole is preferably tolyoltriazole or benzotriazole.

In comparison with using only one of the acid types, the combination of mono- and dicarboxylic acid or its salts provides a synergistic effect when the corrosion protection of metallic surfaces is concerned. The triazole is specifically used as a cupper protection.

Other conventional corrosion-inhibiting components can of course also be included in the heating/cooling fluid according to the invention.

Example

In order to test the heat transfer characteristics, a system in which the liquid which is to be tested is circulating with a constant volume flow under constant pressure was used. This liquid passes a metal coupon onto which a heating device is applied. The temperature of the liquid is kept constant by means of a cooling coil. The temperature of the metal coupon is measured and recorded over time. An increase of the temperature in the metal coupon indicates a relative impairment of the heat transfer ability over the same time.

The liquids which were tested exhibited the following compositions:

INCLUDED COMPONENTS (weight-%)	Reference - Cooling fluid with conventional inhibitor	Test - Cooling fluid with inhibitor according to the invention
Water	49.8	60
Potassium acetate	31.2	31.2
Potassium formate	7.8	7,8
Sodium benzoate	1.1	-
Tolyoltriazole	1.7	-
Borax	0.3	-
Sodium meta-phosphate	1	-
Sodium nitrate	1.8	-
Sodium silicate	0.3	-
Glycerol	5	-
Corrosion inhibitor acc. to the invention	-	1

The following results were obtained for the heat transfer characteristics:

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Test duration (h)	Reference	Reference
	Coupon temperature (°C)	Coupon temperature (°C)
0	170	170
10	181	171
20	183	171
30	184	171.5
40	186	171
45	188	171.5

As is evident from these results, the test liquid, which comprised an addition of a corrosion inhibitor according to the invention, gave a very small increase of the temperature in the

metal coupon over time, something which indicates a maintained effective heat transfer between the metal surface and the fluid. The reference, however, which contained a conventional corrosion inhibitor essentially in accordance with EP 306,972, exhibited a significant increase of the temperature in the metal coupon in the course of time and, accordingly, a relative impairment of the heat transfer ability in the same time period.

This difference is thought to be the result of the corrosion inhibitor in the reference fluid forming a film between fluid and metal surface, which impairs the heat transfer. It is presumed that such a film formation, however, does not take place when utilizing the corrosion inhibitor according to the invention.